Molecular Dynamics prediction of elastic and plastic deformation of semi-crystalline polyethylene

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ABSTRACT: The plastic deformation of a semi-crystalline polyethylene is predicted by a molecular dynamics method. A full-atom model is able to predict the correct amorphous and crystalline phases. Two high molecular weight molecules are involved in these two phases with 3D-periodic conditions. This is one of the first fully coupled model including the main features of the molecular organization. A tensile experiment is applied on the molecular system perpendicular to the lamellae surface. The deformation mechanism inside the amorphous and crystalline phases, and the force evolution, are detailed. This analysis is able to check the effect of details of molecular structure in the amorphous phase on the solid-state rheology. Moreover, a cavitation appears very early in the amorphous phase for all the simulations.

Key words: Molecular dynamics, polyethylene, semi-crystalline, elastic deformation, plastic deformation

1 INTRODUCTION

The molecular structure of polymers and the crystallization conditions strongly act on the semi-crystalline structure and the solid-state rheology. The spherulitic organization results from static crystallization condition during extrusion process and in the core of injected parts. This rheology depends also on the deformation path (traction, shear, compression …). Under traction the non-affine deformation of the spherulite begins in equatorial zones and propagates to the polar zones [1]. This process depends on the deformation path which explains the difference of rheology observed. Decoupled molecular models are able to predict the main features as a function of deformation path with mechanical models of crystalline and amorphous phases [2]. They consider critical shear-stress on shear planes inside crystals and a finite extensibility chain model (Langevin dumbbell) for the amorphous phase [2]. The rheological behaviour must be searched at the molecular level to predict such complex rheology.

A coupled molecular model is necessary to physically describe the deformation mechanism and the rheology. Molecular chains go through thecrystalline and amorphous phases in the initial configuration with a physical path which must include all the key points of the organization. A traction of the equatorial zone is applied by a molecular dynamics model with a full atom description of the polymer chains.

2 MOLECULAR MODEL

2.1 Model construction

The physical modelling of semi-crystalline polymer is a difficult task as an effect of numerous physical constrains which must be applied. Two linear polyethylene chains M= 108 656 g.mol^{-1} (46 570 atoms) must completely contribute to the amorphous

and crystalline phases in the equatorial zone. In the molecular dynamics model these parallel crystalline layers are separated by two amorphous layers. The crystalline content is fixed to 75% as usually observed on that linear polymer, which implies a 3 nm thickness for the amorphous phase with crystalline lamellae 9 nm thick. The chains adopt an all-trans conformation inside the crystalline phase oriented along the lamella thickness. Their organization inside an orthorhombic crystal ($\mathbf{a}$ = 0,74 nm, $\mathbf{b}$ = 0,493 nm, $\mathbf{c}$ = 0,254 nm [3]) implies 72 CH_2 segments inside the thickness. The gyration radius of these molecules corresponds to a random coil.

A statistic of different boundary conditions must be applied to the molecule between amorphous and crystalline phases. The chain path goes through the crystalline and amorphous phases with multiple paths, including chain-foldings, large loops and tie-molecule which connect the crystalline phases and are able to stress under tension the amorphous and crystalline phases [4]. The weight of each contribution is deduced from Monte-Carlo model which lead to controversial results [4-6]. The fraction of tie-molecules varies from 0.1 to 0.5 [4] A wide and a narrow distribution of tie-molecules are considered here, the literature is very poor for this physical parameter. The molecular model respects all the freedom degrees of this molecular organization and applies a Dreiding force-field. The main orientation of chain folding [110] corresponds to known mechanisms of crystallization [7]. The fraction of each contribution is chosen to be consistent with literature.

A 3D periodic condition is applied for olecular dynamic simulations of this semi-crystalline organization. The dimensions $\mathbf{A}$ = 3.7 nm, $\mathbf{B}$ = 3.944 nm and $\mathbf{C}$ = 26 nm are larger than the cutoff of the van der Waals force field (1 nm). The model is built with hyperchem software in successive steps (fig. 1)

- building of a crystal 9 nm thick with molecular segments in an all-trans conformation forming an orthorhombic crystalline phase,
- overlay of two identical parallel crystals (fig.1a),
- creation of a chessboard table to describe the molecular path from the amorphous to the crystalline phase,
- creation of thigh foldings and of loops from the crystalline surfaces (fig.1b, 1c),
- creation of tie-molecule with a known length between two crystals (fig. 1c),
- relaxation of amorphous phase by molecular dynamics (fig. 1e),
- coupling of amorphous and crystalline phases,
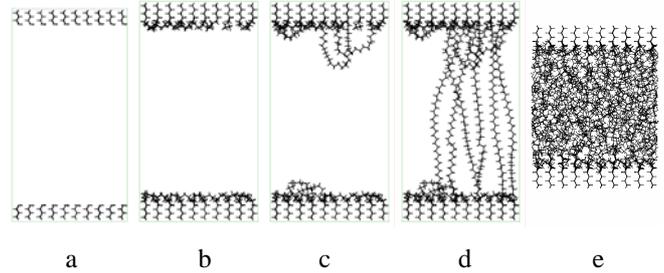- relaxation of complete the system by molecular dynamics.

Fig. 1. creation of amorphous phase : a, crystalline surfaces b, thigh foldings c, loops d, tie-molecules e, relaxation by molecular dynamics

Three models were done with a variation of tie-molecule fraction and their length distribution, which are the parameters not completely known from literature (table 1).

Table 1 : fraction and length distribution of tie-molecules

system	1	2	3
Fraction tie-molecules	0.43	0.17	0.43
Tie-molecules distribution	narrow	narrow	wide

After relaxation, to minimize its energy, these models are stable with a realistic orthorhombic crystalline phase ($\mathbf{a}$ = 0.73 nm, $\mathbf{b}$ = 0.4841 nm, $\mathbf{c}$ = 0.2514 nm).

2.2 Molecular dynamics method

Molecular dynamics simulations have been applied with the DL_POLY software [8] modified in order to apply traction along $\mathbf{C}$ direction. A NPT thermodynamic ensemble (Gibbs) is applied for relaxation and a NσT ensemble (σ stress tensor) for the tensile simulations. N atoms, a pressure (P = 1 bar) and a temperature (T = 27°C = 300 K) are controlled by Berendsen's thermostat and barostat, with 0.5 ps and 10 ps time constants respectively. A Dreiding force-field [9] modified by Dehaudt [10] to produce more realistic parameters of crystalline phase. The bond and interaction potential includes the following contributions :

- bond : $V(r) = 1/2\ k_B(r-r_o)^2$ k_B=700 kcal.mol^{-1}Å^{-2} and r_{oCC}=0.153 nm, r_{oCH}=0.109 nm   (1)

- valence angle : $V(\theta) = 1/2\ k_\theta[\cos(\theta)-\cos(\theta_o)]^2$ k_θ=112.5 kcal.mol^{-1}, θ_o=109.47°   (2)

- torsion angle : $V(\phi) = k_\phi[1+\cos(m\phi-\delta)]$
  $k_\phi = 0.17$ kcal.mol^{-1}, m=3 and δ=0   (3)

- van der Waals $V(r) = C_e \exp(-r/\rho) - C_6/r^6$
  $C_{eCC} = 6740.34$ kcal.mol^{-1}
  $C_{eCH} = 5609.57$ kcal.mol^{-1}
  $C_{eHH} = 1473$ kcal.mol^{-1}
  $C_{6CC} = 780.99$ kcal.mol^{-1}Å^6
  $C_{6CH} = 134.38$ kcal.mol^{-1}Å^6
  $C_{6HH} = 26.10$ kcal.mol^{-1}Å^6
  $\rho_{CC}=0.3571$ $\rho_{CH} = 0.2857$ Å $\rho_{HH} = 0.2778$ Å   (4)

a cutoff of 1 nm is applied for the van der Waals interactions. A 1 fs (10^{-15} s) time-step is applied for this all-atom model and the traction is applied at 0.1 nm/ps which induces a 4.10^9 s^{-1} initial strain-rate on the three models (table 1).

3 RESULTS

3.1 Deformation of semi-crystalline polyethylene

The different steps of deformation of the semi-crystalline polyethylene in the elementary box with a 3D periodic condition can be observed and analyzed as a function of uniaxial strain (fig. 2).
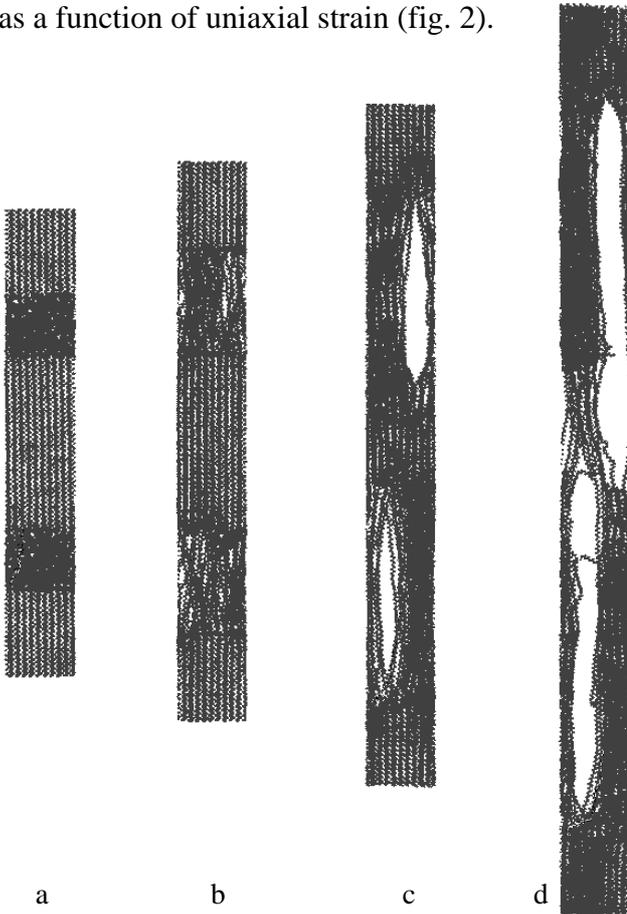
Fig. 2. morphological change during deformation : a, $\lambda = 0$ b, $\lambda = 0.2$ c, $\lambda = 0.5$ d, $\lambda = 1$

All the models basically are deformed in a very similar way. During the first steps the amorphous phase is preferentially strained with an almost unmodified crystalline phase (between fig. 2a 2b). Then the crystalline phase is progressively destroyed. Nanovoids appear for a very low deformation inside the amorphous phase and its size progressively increases then coalesce with others nanovoids (fig. 2c 2d). This amazing phenomenon is unavoidable under atmospheric pressure. It results from a constraint from the crystalline phase. The lateral dimensions **A** and **B** of the crystal and therefore of the amorphous phase remain almost unchanged during most of the traction simulation. The amorphous phase is deformed along the **C** direction and consequently the density of the amorphous phase decreases which leads very early to nanovoids (fig. 2b).

3.2 Solid-state rheology

The stress-strain behavior $\sigma = f(\lambda)$ is a result of the molecular dynamics simulation (fig. 3).
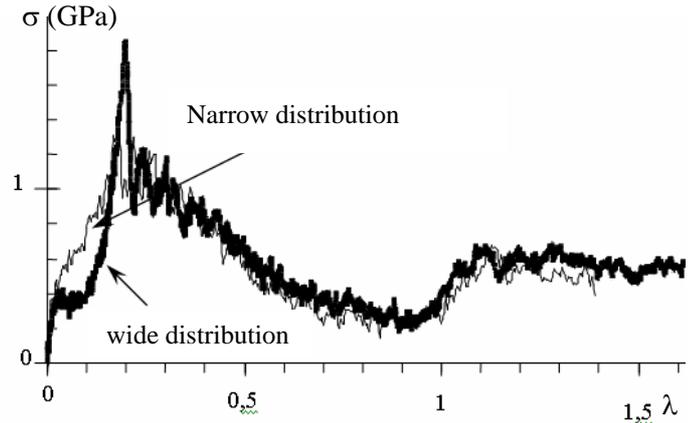
Fig. 3. stress-strain behavior for narrow and wide length distributions of tie-molecules

The stress increases up to a strain $\lambda \sim 0.2$ and suddenly decreases and is followed by oscillations. This decrease results from the destruction of crystals and from the large development of voids (fig. 2c 2d). The behavior under large deformation, above $\lambda = 0.2$, is not representative of sphérolite deformation the deformation is no more confined inside the equatorial zone of the spherulites.

The analysis will be focused to small deformation. The peak $\sigma_{max} = 1,9$ GPa is the yield stress for plastic deformation of the crystal inside a model including 43 % of tie-molecules. This yield-stress is reduced to 0.8 GPa for 17% of tie-molecules. A decrease by a factor 2.4 of tie-molecules reduces the yield-stress by only a factor 1.4. A so large value is not due to the large amount of tie-molecules but mainly to the very high strain-rate (10^9 s^{-1}). Simulations with different strain-rates follow a

power-law model with a strain-rate exponent n = 0.09 very similar to the value found from experiments done up to 10^{-3} s^{-1}. The regression under this very large strain-rate range shows a convergence of predicted yield-stress with the experimental value.

3.3 Effect of the length distribution of tie-molecules

The length distribution of tie-molecules directly acts on the deformation mechanisms and on the rheology under low macroscopic deformation. All the chains of a narrow distribution are almost deformed in the same way at the same time by uncoiling up to their extensibility limit. From that point the plastic deformation of the crystals begins (fig. 4).
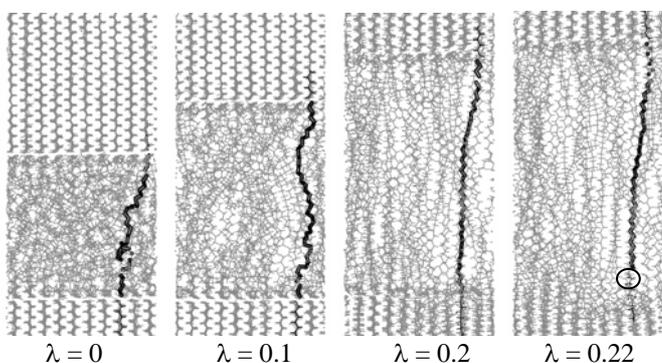

$\lambda = 0$ $\lambda = 0.1$ $\lambda = 0.2$ $\lambda = 0.22$

Fig. 4. deformation mechanism of a tie-molecule as a function of deformation , ◯ chain pulling-out from the crystal

The constant stress curve observed from 0.03 to 0.1 for the narrow distribution is explained on that way (fig. 3). It is the behavior of a Langevin chain (fig. 4). A wide length distribution of tie-molecules implies that short chains are deformed very early and pull-out some segments initially inside the crystalline phase. This phenomenon takes progressively place for longer tie-molecules and the stress progressively increases. The constant stress no more exists. This result implies that plastic deformation appears very early and progressively before the macroscopic yield stress.

4 CONCLUSIONS

A direct fully-coupled simulation of semi-crystalline polymer deformation can be done by molecular dynamics method. The model building gives an insight of the semi-crystalline organization and on parameters which are not measured by experiments up to now. The subtle deformation mechanisms can be followed and the resulting solid-state rheology are deduced at the same time. The nanovoid formation is a direct consequence of the molecular organization. Further works on other semi-crystalline polymers should be helpful to strength the present conclusions and a multiscale modeling is necessary to predict the rheology under a larger strain domain. Molecular dynamics is the elementary level for a coupling with mesoscopic modeling of a spherulite.

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